Parameter optimization and mechanism research of enhanced coagulation treatment for Yuquan River water

Qianshu Sun, Shuang Zhao, Yubo Yan, Wenlin Jia and Weihua Yang

ABSTRACT

As one of the drinking water sources for Xuzhou city, Yuquan River has been polluted seriously in recent years. In this paper, enhanced coagulation technology was selected and various parameters (coagulant species, dosage, solution pH and coagulant aid species) were optimized for Yuquan River water treatment. Turbidity and UV_{254} removal rate were calculated to assess coagulation efficiencies, and meanwhile floc generation kinetics, zeta potential and scanning electron microscope (SEM) spectra were measured to study the coagulation mechanism. Results indicated that the coagulation effect of polyaluminium chloride (PAC) on Yuquan River water was better than that of aluminium sulphate (AS), and its optimal dosage was 20 mg/L. Flocs produced by PAC also exhibited larger size and faster growth velocity than those of AS. Moreover, the applicable initial pH range for Yuquan River was 6.0–9.0, and the optimal coagulation efficiency was observed at pH 7.0. When PAC or AS was selected as coagulant, the application of sodium alginate (SA) could improve turbidity and UV_{254} removal due to its adsorption bridging role. In addition, coagulation efficiency could be enhanced in an AS coagulation system when polyacrylamide (PAM) was dosed as coagulant aid.

Key words | enhanced coagulation, flocs properties, pH, polyacrylamide, sodium alginate, Yuquan River water

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INTRODUCTION

The deterioration of urban water quality has become more and more serious due to the emission of industrial wastewater, municipal domestic wastewater, agricultural wastewater and surface runoff water. More and more lakes and rivers have been polluted to a great extent, and one of them is Yuquan River. It is one of the drinking-water sources located in Xuzhou city, China, which originates from Chu River and flows eastward from Songshan Road to Kuihe River, through the centre of Tongshan district in Xuzhou city. More importantly, it runs through the campus of Jiangsu Normal University, which provides a learning and rest environment for students. In addition, it supplies teaching-experiment water samples for students who major in environment engineering, bioscience and chemistry. However, with domestic sewage and industrial sewage discharging into Yuquan River, its water quality has been declining dramatically: initial turbidity and UV_{254} absorbance achieved about 10 NTU and $0.05\ cm^{-1}$. It is urgent to improve the water quality of Yuquan River to make it clear, and further improve the learning and living environment for students and inhabitants.

As we all know, coagulation is the most commonly used pre-treatment method for colloid particle removal in the surface water treatment process. However, the efficiency of organic removal by coagulation is still less than satisfactory. Therefore, enhanced coagulation, which refers to the process of improving the removal rate of organic matter under the condition of the conventional coagulation process, has been used widely in the water treatment process in recent years (Wu *et al.* 2005). Compared with conventional technology, enhanced coagulation could remove natural organic matter (NOM)

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in water effectively and guarantee the effluent index would meet drinking water quality standards. Generally, enhanced coagulation has three primary measures: adjusting pH of the raw water, raising dosage of coagulants and applying late-model coagulant or coagulant aid (Yan *et al.* 2008; Zhu *et al.* 2016; Sillanpää *et al.* 2018). At present, aluminium sulphate (AS) and polyaluminium chloride (PAC) are considered as two inorganic metal or pre-hydrolysed metal-ion coagulants, which are typical and widely used in both water and sewage treatment plants (Duan & Gregory 2003; Jiang 2015). The coagulation mechanisms of alum salts mainly include charge neutralization, interparticle bridging and entrapment processes (Mao *et al.* 2013). The confirmation of the dominant mechanism depends on water quality, pH value, particle concentration and disturbance intensity of water flow, etc. However, a number of drawbacks of residual aluminium in effluent have been reported recently. Above all, it may cause many kinds of disease in the human body (Hu *et al.* 2013), and shows an exacerbated tendency with the increase of alum dosage. Therefore, increasing alum dosage is not a preferred method in an enhanced coagulant process. In recent years, application of effective coagulant aids has been proposed to solve the above problems, which can improve coagulation efficiency, decrease the concentration of residual Al in effluent water and reduce the cost of water treatment (Hu & Wu 2016; Sillanpää *et al.* 2018). Coagulant aids play a role in accelerating the flocculation process or strengthening flocs, which make the effluent easier to be filtered. According to their action mechanism, coagulant aids can be divided into three categories: pH adjusting agents, floc structure conditioners and oxidizing agents. Synthetic polymers, such as cationic polyacrylamide (PAM), became the most common coagulant aid due to their large molecular weight. PAM is an effective flocculant for separating various suspended ions from wastewater. It is a kind of white powder with many functional groups which has an excellent coagulation aid effect (Huang *et al.* 2016). Sodium alginate (SA) is a kind of polysaccharide carbohydrate, which can be extracted from kelp or *Sargassum*, and its average molecular weight can exceed 500,000 Da. It is widely used in medicine, food and other industries, and has become a new-style coagulant aid in the wastewater treatment process in recent years (Wu *et al.* 2012; Yang *et al.* 2016).

In conclusion, there are three problems which need to be solved for the treatment of Yuquan River: (1) how to select the best kind of coagulant that is suitable for Yuquan River and further enhance its treatment efficiency by the optimization of operating conditions; (2) how to extend the scope of alum coagulant application by pH adjustment in the water treatment process; (3) how to reduce coagulant dosage by using a coagulant aid on the premise of meeting national emission standards. In this study, PAC and AS were used to coagulate Yuquan River water, and the optimum dosage coagulants and initial solution pH were determined. SA and PAM were used as coagulation aids and the best working condition of the composite coagulants was investigated. In addition, the major coagulation mechanism under various conditions was discussed.

MATERIALS AND METHODS

Chemicals and raw water

Chemicals used in this research included $Al_2(SO_4)_3{\cdot}18H_2O$, $AlCl_3{\cdot}6H_2O$, HCl, NaOH, PAM and Na_2CO_3, which were all purchased from Sinopharm Chemical Reagent Co., Ltd, Beijing. SA was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. All solutions were prepared with deionized water and stored at 4 °C. Raw water samples were collected from the Yuquan River in Xuzhou city, Jiangsu province, and the characteristics of the source water are shown in Table 1.

Coagulants and coagulant aids

AS and PAC were selected as coagulants in this research. A certain amount of $Al_2(SO_4)_3{\cdot}18H_2O$ was dissolved directly in deionized water to prepare a solution with aluminium

Table 1 | Water quality of Yuquan River water

Water quality index	Value
Temperature	14–16 °C
pH	7.87–8.86
Turbidity	6.78–10.70 NTU
UV_{254}	0.0455–0.0496 cm^{-1}
Zeta potential	−10.56–−6.43 mV

concentration of 4.0 g/L. PAC solution was prepared as follows: 8.948 g of $AlCl_3$•$6H_2O$ was dissolved in 100 mL deionized water firstly, and then 1.964 g of Na_2CO_3 was added to the solution slowly with persistent stirring. After all the Na_2CO_3 was added, the solution was stirred continuously for 2 h until it became transparent. Finally, 1.292 g of Na_2HPO_4•$12H_2O$ was added as stabilizer. The concentration of PAC was 10 g/L and the B value (molar ratio of OH^- and Al^{3+}) was 1.0.

PAM and SA were selected as coagulant aids. The PAM solution of 1.0 g/L was obtained by dissolving PAM in deionized water directly and then keeping it stirred for 4 h. However, due to the inferior water-solubility of SA, the water bath temperature was set at 70 °C to prepare the SA solution. The pH of the deionized water (1 L) was adjusted to 3.0, and then 1.0 g SA was dosed with constant stirring for 3 h. When all the SA was dissolved, the pH of the water solution was adjusted to neutral.

Jar-test

Coagulation tests were conducted by a jar-test apparatus (MY3000-6, Wuhan Meiyu Instrument Co., Ltd, China). One litre of Yuquan River water was decanted into a beaker after mixing uniformly, and the procedure set on the mixer was as follows: the water sample was stirred at 300 rpm for 30 seconds and then a certain amount of coagulant was added. After rapid stirring for 60 s, coagulant aids were dosed and the rate of agitation was reduced to 40 rpm for a duration of 15 min, followed by 30 min of static settlement. Afterwards, a sample from 2 cm below the surface was collected and measured. Part of the sample was taken to measure residual turbidity and zeta potential directly by using a 2100Q turbidimeter (Hach, USA) and Zetasizer NanoBrook 90 Plus PLAS (Brookhaven, USA). The remaining samples were filtrated by a piece of fibre membrane (0.45 μm) to measure UV_{254} absorbance (Perkin, China). In order to ensure the accuracy and reliability of this study, all experiments were repeated three times.

Growth and sedimentation process of flocs

As the coagulation experiments proceeded, a Mastersizer 2000 (Malvern, USA) was used to monitor floc size by the method of dynamic light-scattering. The coagulation process was set as follows: PAC was added firstly with rapid mixing (300 rpm) for 30 s, followed by SA dosing and stirring for 1 min with the same mixing speed (micro-floc generation phase), and then slow mixing (40 rpm) for 15 min (floc growth phase) was performed. In this process, samples were collected and then added to the optical unit of the Mastersizer by injector. The nozzle of the syringe should be larger than 0.5 cm to avoid the breakage of flocs before measurement. The median volumetric diameter (d_{50}) was recorded and meanwhile, the particle size distribution of flocs from 0 to 1,000 μm was also analysed. In this study, size measurements of flocs were taken each 60 s during the coagulation process. The floc growth characteristic was described by the value of the growth rate (Gr), which was calculated as follows:

$$\text{Growth rate} = \frac{\Delta size}{\Delta time}$$

After sedimentation for 1, 3, 5, 10, 15 and 20 min, samples were collected to measure residual turbidity to evaluate the settling ability of flocs. In theory, lower residual turbidity indicates better flocs-settling ability (Zhao *et al.* 2015). It is worth noting that the beaker should be kept steady as much as possible when sampling.

RESULTS AND DISCUSSION

Determination of the optimal coagulant and dosage

Appropriate kind of coagulant and dosage could enhance the properties of effluent water, and meanwhile reduce the cost of water treatment. For the purpose of confirming a suitable coagulant for Yuquan River water, coagulation optimization tests were conducted, and AS and PAC were used as coagulant separately to study the coagulation effect under raw-water pH conditions. Figure 1 shows that with AS and PAC dosage increasing, turbidity removal kept stable and then increased steadily in the PAC coagulation system, and eventually turbidity removal exceeded 70%, while significant reduction was observed when AS was used as coagulant. Therefore, PAC had better turbidity

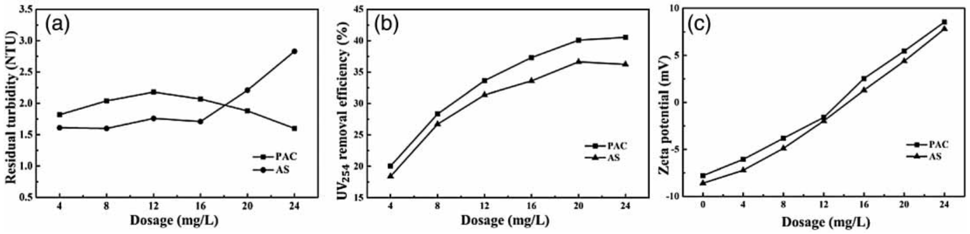

Figure 1 | Effect of coagulant dosage on coagulation performance: (a) turbidity removal; (b) UV_{254} removal; (c) zeta potential.

removal efficiency than AS. For UV_{254} removal efficiencies, results showed a gradually rising tendency at lower coagulant dosage, which was consistent with the increase of zeta potential (Figure 1(c)), since both AS and PAC could form positively charged products in the coagulation process. However, the growth trends reached a platform when coagulant dosage was larger than 20 mg/L, and further increase in the dosage of AS and PAC could not obviously enhance organics removal. The maximum UV_{254} removal (36.64% for AS and 40.09% for PAC) was achieved when the aluminium dosage was 20 mg/L, where zeta potential came up to 4.38 mV and 5.45 mV respectively.

Figure 1(c) shows that zeta potential ranges from −10 mV to 10 mV, implying that the system was unstable and colloidal particles were easy to aggregate and settle down. PAC possessed a good coagulation effect although it did not achieve the isoelectric point, which signified that PAC mainly acted on colloidal particles and organic matter molecules through net trapping, sweeping and adsorption bridging. References also pointed out that when charge neutralization was the only coagulation pathway, the change of zeta potential showed a good correlation with coagulant dosage (Li *et al.* 2009). As a result, when zeta potential approaches zero, the best coagulation efficiency should be achieved (Pefferkorn 2006; Li *et al.* 2009). Therefore, data in this study indicated that for PAC or AS coagulant, charge neutralization was not the single mechanism. Since the natural water was alkaline ($pH = 7.87–9.86$), amorphous hydroxide precipitates might be generated in large quantities (Pefferkorn 2006; Zhao *et al.* 2012). In addition, adsorption precipitation might lead to charge neutralization in this research. Therefore, although zeta potentials were less than zero, the turbidity removal was still at a high level at low coagulant dosages. In summary, the coagulation effect of PAC on Yuquan River water was better than that of AS, and the optimal coagulant dosage was 20 mg/L.

Floc growth and settling characteristic

The settling velocity of small particles is always slower than that of large particles, which generally causes lower removal efficiency of coagulation (Wei *et al.* 2010; Zhang *et al.* 2017). Furthermore, particle transport mechanisms might be changed due to the reduction of floc size (Aguilar *et al.* 2003; Xiao *et al.* 2010). A larger growth rate of flocs can shorten coagulation time and means a smaller coagulation tank, which is a great advantage in industrial practice (Yu *et al.* 2009; Chekli *et al.* 2015). In the coagulation process, the settling speed after floc formation is also critical, and affects water treatment cost. In actual operation, with the faster settling speed of flocs, hydraulic retention time and operation cycle will be shorter and thus the treatment capacity per unit time can be improved. In this section, floc size, growth rate and settling ability were all researched with AS and PAC coagulant dosages of 20 mg/L, and Figure 2 shows the experimental results.

For both AS and PAC, negative charges on colloidal particles could be neutralized quickly and effectively when the coagulant was added, and then micro-clusters formed. The unstable aluminium species in AS and PAC were hydrolysed (including monomers and dimers), which contributed to the formation of precipitated solids and synthetic compounds or co-precipitate adsorption (Bi *et al.* 2004). Floc sizes grew rapidly in the first 5 min as coagulant was dosed to the Yuquan River water sample, and then it achieved a balance stage between floc formation and breakage, which exhibited a steady-state platform of floc size (Figure 2(a)). In the steady phase, the size of flocs generated by PAC reached 435.6 μm, which was much larger than that of AS (359.6 μm).

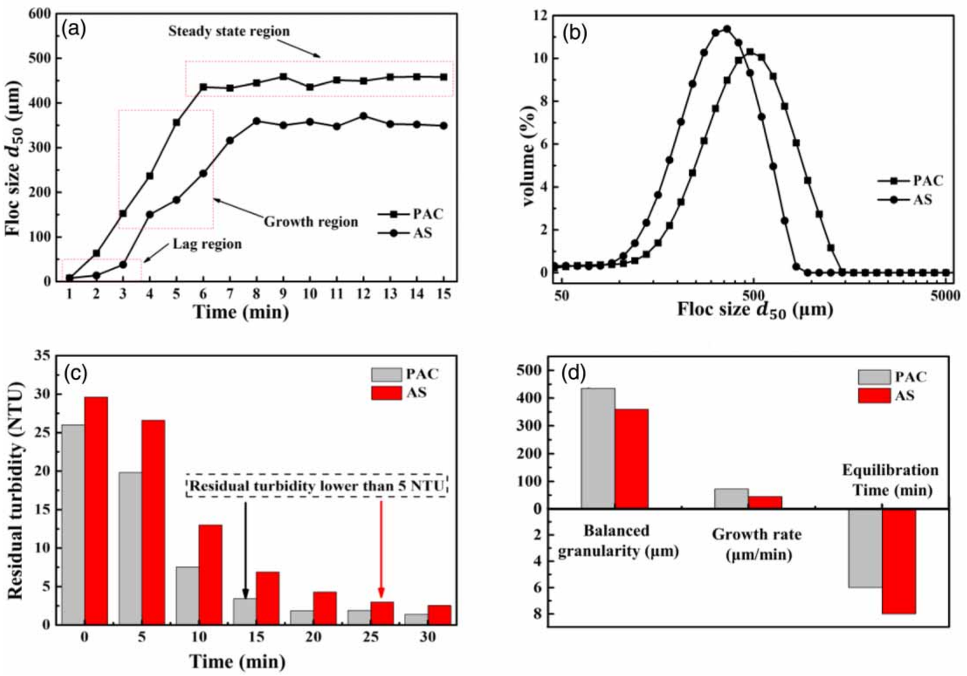

Figure 2 | Floc growth and settling characteristics: (a) growth rate; (b) size distribution; (c) settling ability; (d) growth characteristics.

Figure 2(b) shows that the floc size distribution peak of PAC was on the right side of AS, which is in accordance with the conclusion of Figure 2(a). In addition, the equilibrium time was only 6 min in the PAC coagulation system, while when AS was used, it needed 8 min to reach the steady-state platform. As a result, the floc growth rate of PAC was much larger than that of AS. The dominant mechanism of AS was charge neutralization, while a variety of macromolecule hydrolysis products could occur when PAC was dosed. Since the Yuquan River water sample was alkaline, the precipitation and adsorption bridging roles of amorphous hydroxide were significant, and could accelerate the bridging process among microflocs, which would further aggregate into larger flocs within a short time. A previous study showed that bridging and sweeping flocculation produced much larger flocs than charge neutralization (Xiang & Liu 2005), which is consistent with results in this section.

Precipitated flocs were collected to be freeze-dried, and then sprayed with a thin layer of gold. Floc morphology and microstructure were researched using a scanning electron microscope (SEM) in this paper (Figure 3). Results showed that floc structure produced by AS was more compacted, which contributed to higher positive charges of AS and the weak repulsive forces between particles within flocs. However, floc structure formed by PAC was more porous. This should be attributed to the adsorption and bridging mechanism of PAC, which resulted in the formation of flocs with open structure. The result was in accordance with the conclusion of Yu *et al.* (2009), who found that Al hydrolysate produced by PAC could absorb and entrap contaminants and resulted in fluffy floc structures. In addition, flocs had settled completely after 15 minutes in the PAC coagulation system, while they needed 25 minutes in the AS coagulation system (Figure 2(c)). After 30 min of precipitation, residual turbidity was only 1.38 NTU and 2.55 NTU when the two coagulants were used. This indicated that PAC had a strong adsorption bridging ability. The bigger size, faster growth rate and better settling ability of flocs produced by PAC means a shorter coagulation process. Consequently, PAC was the optimal coagulant for the Yuquan River water in terms of floc characteristics.

Effect of pH on coagulation effect

The influence of initial pH on coagulation efficiency was studied at lower dosage (8 mg/L), optimal dosage (20 mg/L)

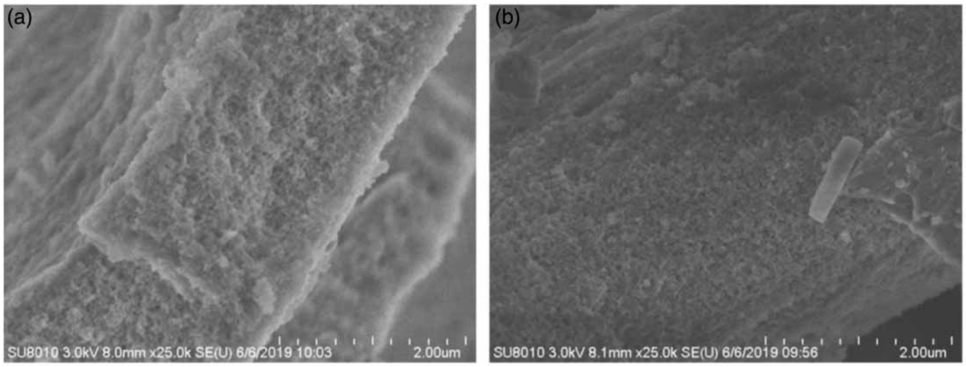

Figure 3 | SEM image of flocs generated by: (a) AS coagulant; (b) PAC coagulant.

and higher dosage (24 mg/L) of PAC coagulant, respectively (Figure 4).

At lower dosage, when the pH value was lower than 6.0, turbidity removal increased obviously with the increase of pH value, and then reached a stable level. At optimal and higher dosages, turbidity removal efficiencies were both increased evidently when the pH value ranged from 4.0 to 7.0, and achieved 79.15% and 82.54% at pH 7.0. This suggested that colloidal protection resulted in high turbidity in acidic conditions. For PAC, the optimum initial pH range was 6.0–9.0, which indicated that PAC could work well in a wide range of initial pH conditions. UV_{254} removal of PAC reached the maximum at pH 6.0, and the removal efficiencies were both high at pH 6.0 and 7.0. Figure 4(d) shows that the change of pH had a great influence on zeta potential: under acidic conditions, zeta potential increased significantly with rising pH, while a continuously decreased trend was observed when pH was higher than 6.0. It has been reported that positive polymer hydrolysates or $Al(OH)_3$ would be hydrolysed in weak acidic and neutral conditions, which could act on colloidal particles and organic molecules in water by

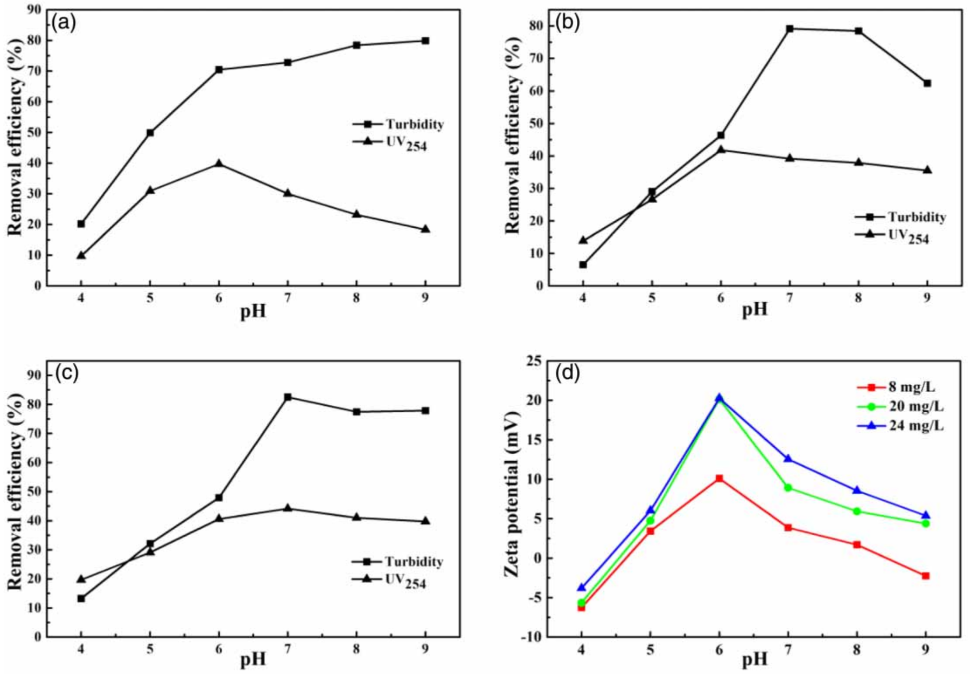

Figure 4 | Effect of raw water pH on coagulation performance for PAC: (a) 8 mg/L; (b) 20 mg/L; (c) 24 mg/L; (d) zeta potential.

adsorption bridging and sweeping nets (Wang *et al.* 2009). The coagulant was easy to combine with H^+ to form complex and other substances under lower pH conditions. Aluminium hydroxide and other substances would occur under higher pH conditions because the coagulant combined with OH^-, which made it difficult for the coagulant to combine with pollutants and reduced the coagulation treatment effect (Zhou *et al.* 2000).

Figure 5 shows that when AS was used, coagulation efficiency varied similarly with that of PAC coagulant. When AS doses were 20 mg/L and 24 mg/L, optimal organic removal rates were both obtained at pH 7.0 and reached 40.09% and 42.49%, separately. It could be explained that Al^{3+} was the main hydrolysate of AS below pH 5.0, and it had poor adsorption bridging and sweeping net trapping ability, causing a poor coagulation effect (Sun *et al.* 2019). With pH ranging from 6.0 to 8.0, high polymeric hydrolysates and $Al(OH)_3$ can adsorb and co-precipitate pollutants in water (Guo *et al.* 2015; Huang *et al.* 2017). As pH exceeds 8.0, Al is converted to $[Al(OH)_4]^-$, which is difficult to bind to pollutants (Chu *et al.* 2016). Therefore, it can be generalized that the optimal pH for AS and PAC was 6 and 7 for Yuquan River water treatment. The best coagulation efficiency was reached when solution pH was 7.0 and PAC dosage was 20 mg/L.

Effect of SA addition on coagulation efficiency

SA was applied as coagulant aid in this section, and coagulant dosage and solution pH were fixed at 20 mg/L and 7.0 according to the above optimization results. Since inappropriate dosage of coagulant aid would deteriorate coagulant performance, SA dosages of 0.1, 0.3, 0.5 and 0.7 mg/L were selected, and the variation of turbidity, UV_{254} removal and zeta potential with various SA dosages are shown in Figure 6.

As can be seen, turbidity removal efficiency could be obviously improved by SA addition: the turbidity removal was up to 87.69%, whereas obtained by PAC alone it was only 78.21% (Figure 6(a)). Turbidity removal of AS–SA showed the same variation trend as PAC–SA (Figure 6(b)). The result was in accordance with a previous study by Wang *et al.* (2009) who found that coagulation efficiency could be improved when the polymer was used in association with conventional coagulants. This was attributed to the adsorption bridging role of SA, and it was considered

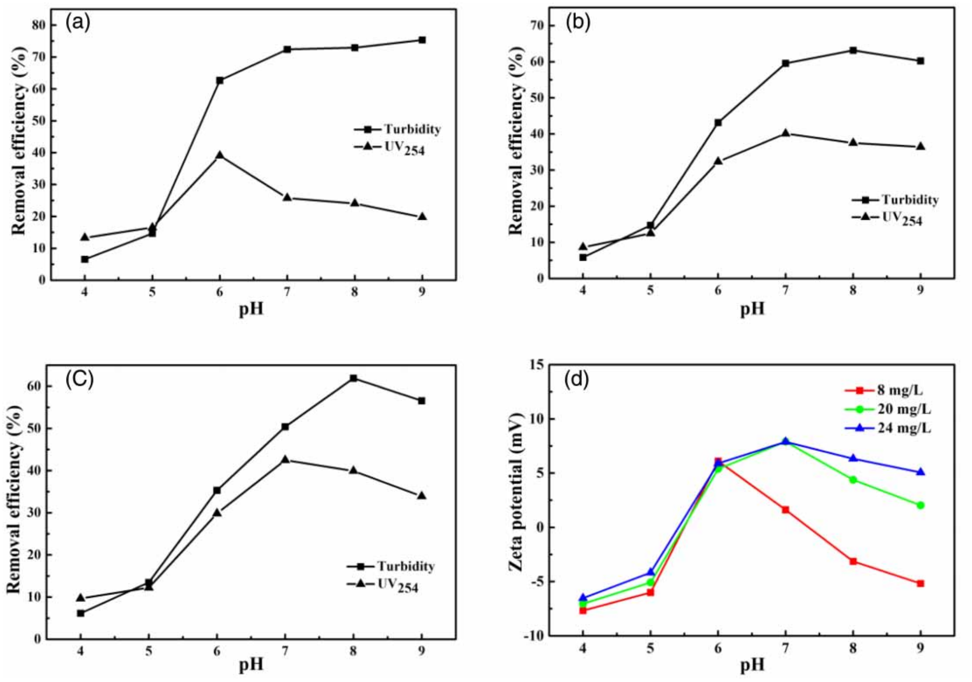

Figure 5 | Effect of raw water pH on coagulation performance for AS: (a) 8 mg/L; (b) 20 mg/L; (c) 24 mg/L; (d) zeta potential.

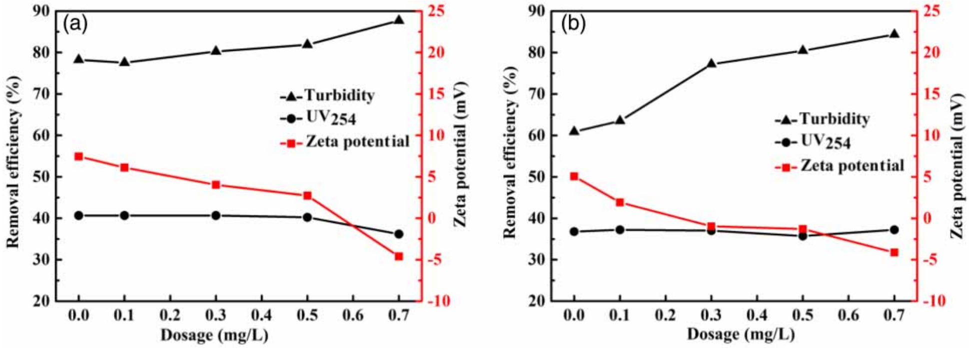

Figure 6 | Effect of SA dosage on coagulation performance: (a) PAC coagulant; (b) AS coagulant.

as the major and effective mechanism which greatly affected the coagulation behaviour of PAC–SA and AS–SA. When PAC or AS was dosed firstly, hydrolysates neutralized negative charges quickly, which weakened repulsion forces between colloids to generate microflocs. Afterwards, SA was dosed and effectively attached to the microfloc surfaces. The long carbon chains of SA promoted a bridging effect among the suspension colloid particles, which generally produced larger flocs with better settling ability. Therefore, better turbidity removal efficiency could be obtained. However, the application of SA could not enhance and even reduced the removal of UV_{254} when superfluous SA was used. As can be seen, UV_{254} removal of PAC–SA and AS–SA at the SA dosage of 0.7 mg/L was 36.18% and 37.17%, whereas the UV_{254} removal achieved by PAC and AS alone was 40.67% and 36.80% respectively. In addition, zeta potential decreased as SA dosage increasing, which indicated that SA could enhance negative charges and cause rejection among colloidal particles, which hindered the aggregation of microflocs. Therefore, when excessive negatively charged SA was dosed, the strong repulsion between particles inhibited the growth of flocs, and the coagulation effects became worse (Zhao *et al.* 2014). On the premise of low coagulant cost and satisfactory coagulation performance, the optimum dosages of PAC and SA were fixed at 20 mg/L and 0.5 mg/L.

Effect of PAM addition on coagulation performance

PAM was used as coagulant aid in this section and a series of dosages of 0.1, 0.3, 0.5 and 0.7 mg/L were selected for study. Coagulant dosage and solution pH were fixed at 20 mg/L and 7.0, and the variation of turbidity, UV_{254} removal effect and zeta potential with various PAM dosages are shown in Figure 7.

As can be seen from Figure 7(b), when AS was applied as coagulant, PAM addition improved the removal efficiency of turbidity and UV_{254}. Especially for the 0.3 mg/L PAM addition, the turbidity removal rate was up to

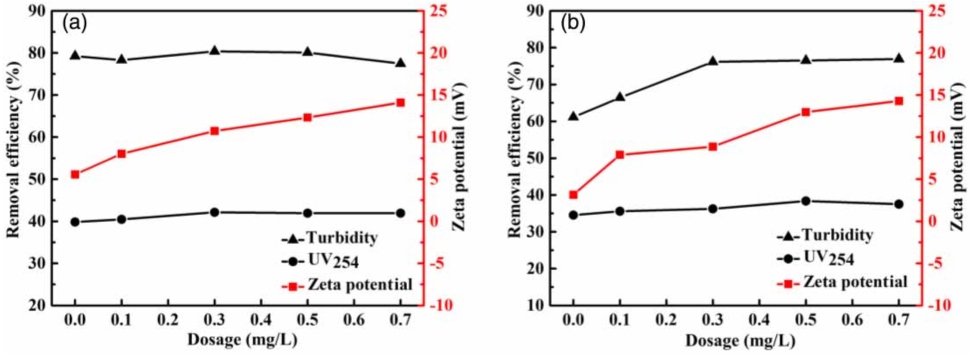

Figure 7 | Effect of PAM dosage on coagulation performance: (a) PAC coagulant; (b) AS coagulant.

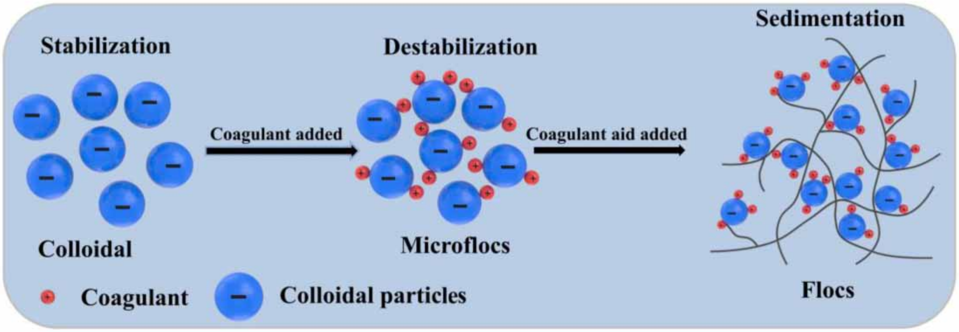

Figure 8 | Mechanism of enhanced coagulation process with coagulant aid application.

76.15%, whereas the removal obtained by AS alone was only 61.15%. Previous research showed that a cationic coagulant aid had a high charge density of cations and long chains, which could exert a bridging effect of charge neutralization and adsorption bridging to a great extent, which could improve the removal rate of turbidity and UV_{254} significantly (Chu *et al.* 2016). In addition, as shown in Figure 8, the molecular weight of PAM used in this experiment was 8,000 kDa, which contributed to a strong bridge-aggregation effect to improve coagulation efficiency. However, coagulation efficiency exhibited a little downtrend when PAM dosage was over 0.3 mg/L. It could be explained that when PAM was further dosed, high positive charges of flocs repelled each other, which inhibited the growth of flocs and consequently reduced the coagulation efficiency. Additionally, Figure 7(b) shows that zeta potential was improved gradually as PAM dosage increased. However, Figure 7(a) shows that when PAM was applied with PAC coagulant, turbidity and UV_{254} removal efficiency could not be further enhanced. Therefore, the optimal dosage for Yuquan River water treatment was 20 mg/L of PAC without the need for additional PAM. But when AS was used as coagulant, 0.3 mg/L PAM could be added to enhance turbidity and organics removal efficiencies.

CONCLUSION

(1) The coagulation effect of PAC for Yuquan River water was better than that of AS, and its optimal dose was 20 mg/L. The dominant mechanism of PAC was net trapping, sweeping and adsorption bridging, which contributed to bigger sizes, faster growth rates and better settling ability of flocs.
(2) The optimal solution pH for Yuquan River water treatment was 6.0 and 7.0 for AS and PAC coagulant, and the highest coagulation efficiency was achieved when the solution pH was 7.0 with 20 mg/L PAC application.
(3) When 0.5 mg/L SA was applied as coagulant aid, coagulation efficiency was much better than that of PAC or AS used alone.
(4) PAM addition could improve coagulation efficiency in the AS coagulation system, and its optimal dosage was 0.3 mg/L. But when PAM was applied with PAC coagulant, removal of turbidity and UV_{254} could not be further enhanced, and there is no need to add any PAM in the treatment process.

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